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## CONTENTS

## ABSORPTION OF LIGHT AND HEAT RADIATION BY SMALL SPHERICAL PARTICLES

### I. ABSORPTION OF LIGHT BY CARBON PARTICLES[1]

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### Abstract

From Mie's classical theory of the action of small spherical particles on plane waves of light, the expression giving the loss of light due to absorption and scattering is reduced to the formula involving only Bessel functions of orders given by half integral values. The result is used for calculating the absorption by small carbon particles whose diameter is comparable with the wave-length of the incident light, particles that can be measured only by interference methods. When the diameter is less than $0.2\ \mu$ the coefficient of absorption decreases toward the red end of the spectrum. The reverse is true for $0.3$ and $0.4\ \mu$ particles.

### Propagation of a Plane Wave of Light past a Spherical Particle

When a small spherical particle is placed in the path of a plane wave of light, a fraction of the radiation striking the particle is returned along different directions into the outer medium, either before or after penetration of the boundary surface; the rest of the radiation is absorbed by electric conduction currents in the particle. On the boundary surface separating the particle from the surroundings, the electric and magnetic forces in the outer medium merge into the components produced by the wave inside the sphere.

The disturbance caused by the particle depends in the first place on the ratio $2a/\lambda$ between the diameter of the particle and the wave-length of light, and in the second place on the optical properties of each medium. When the diameter of the particle is large in comparison with the wave-length, the vibrations transmitted along a given direction from various points of the particle surface may possess appreciable phase differences, so that patterns with alternate dark and bright zones are produced around the obstacle. The phase difference between the vibration transmitted directly through the centre of the sphere and the vibrations transmitted, for instance, from the two poles at the end of a diameter perpendicular to the direction of propagation of the wave, may be such that behind the particle the light is either strengthened or extinguished. On very small particles, on the other hand, the vibrations of all the points on the surface are approximately in phase, even

after more than one complete passage through the particle, and the main result is radiation of light in all directions rather than the formation of distinct beams of light.   Close to the direction of propagation large phase differences are then found only at points so remote from the small sphere that the intensity has become negligible.

The main complication with respect to the better known diffraction observed near sharp edges or behind small opaque discs is that in the case of spherical particles the phase differences and amplitudes depend not only on the path traversed but on the nature of the particle, that is, whether it consists of a dielectric or a conductor.   When the sphere is formed of an ideal conductor the small dimensions prevent it from acting as an impenetrable barrier or sink submerged in the light.   Neither does the particle behave as a multitude of elementary sources of light, all vibrating in phase and allowing the resultant effect to be obtained by drawing the spherical wavelets according to Huygen's principle.

But whether the particle is opaque or transparent, in so far as the vibration observed along a given direction is the resultant of the vibrations propagated from points inside and outside the sphere, the diffraction due to large particles and the scattering by particles with a diameter smaller than the wave-length of light in the surrounding medium are both subject to the laws expressed by Maxwell's equation of the electromagnetic field (2).

In the calculation of the amplitudes for the diffracted or scattered wave that reaches a given point, the spherical particle is placed at the origin of a system of co-ordinates consisting of three axes $(x, y, z)$ at right angles (Fig. 1). The position of any point is expressed by its distance $\rho$ from the centre, or better by the much enlarged distance $r = 2\pi\rho m/\lambda$, where $m$, the square root of the dielectric constant, is the refractive index at that distance ($m_n$ inside the particle, $m_0$ outside the particle), and $\lambda$ is the wave-length measured in the medium concerned (5).   All over the surface of the particle, $r$ assumes the two distinct values $\alpha = 2\pi a m_0/\lambda$ or $\beta = 2\pi a m_n/\lambda$; the first value holds when the point is considered to belong to the inner medium, and the second, when to the outer medium.   The azimuth, $\theta$, or co-latitude, of the point, measured between the vertical axis $x$ and the line joining the point to the origin, and the longitude $\phi$, counted from axis $y$ in the plane $(y, z)$, serve as the second and third co-ordinates of the point.   A plane wave of light of frequency $f$ is assumed
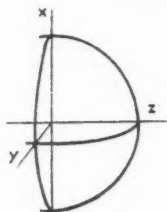


FIG. 1.   *System of co-ordinates x, y, z, chosen for the small sphere.*

to advance toward the centre along the axis $z$ through a medium in which the wave-length is $\lambda/m_0$ and the magnetic permeability $\mu$. If the electric vibrations of this incident wave take place parallel to axis $x$ in the plane $(x, z)$, the equations of the components along the three axes $(x, y, z)$ are

$$e_x = \epsilon^{2\pi i f t + 2\pi i m_0 z/\lambda} \qquad\qquad h_x = 0$$

$$e_y = 0 \qquad\qquad h_y = -\sqrt{\frac{k}{\mu}}\ \epsilon^{2\pi i f t + 2\pi i m_0 z/\lambda}$$

$$e_z = 0 \qquad\qquad h_z = 0$$

The amplitude of the incident vibration is taken as unity.

When applied to alternating currents represented by $E\epsilon^{2\pi i f t}$ and $H\epsilon^{2\pi i f t}$ Maxwell's equation for the amplitude of the electrical vibrations along the directions $(r, \theta, \phi)$ becomes

$$E_r r^2 \sin\theta = \frac{\partial(r\sin\theta M_\phi)}{\partial\theta} - \frac{\partial(rM_\theta)}{\partial\phi}$$

$$E_\theta r \sin\theta = \frac{\partial M_r}{\partial\phi} - \frac{\partial(M_\phi r \sin\theta)}{\partial r}$$

$$rE_\phi = \frac{\partial(rM_\theta)}{\partial r} - \frac{\partial M_r}{\partial\theta}$$

The expression

$$M = -\frac{if\mu\lambda H}{m}$$

is used in place of the component $H$ of the magnetic field.

A second similar group of equations is valid for the amplitudes of the components of the magnetic field $M_r$ along the radius, $M_\theta$ along a meridian circle, and $M_\phi$ along a circle of latitude. Elimination of the other variables leads to the equation

$$\frac{\partial^2(r^2 E_r)}{\partial r^2} + \frac{1}{\sin\theta}\ \frac{\partial}{\partial\theta}\left(\sin\theta\ \frac{\partial E_r}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\cdot\ \frac{\partial^2 E_r}{\partial\phi^2} + r^2 E_r = 0$$

and to a perfectly similar equation in which $M_r$ replaces $E_r$. It is assumed that a solution for $E_r$, and consequently also for $E_\theta$ and $E_\phi$, exists in the form of a product, or rather an infinite series of products of two functions, the first one a function of the distance $r$ only, the second a function of the angles $\theta$ and $\phi$,

$$E_r = \frac{K_\nu(r)}{r^2}\ P_\nu(\theta, \phi),$$

where the subscript $\nu$ is any whole number different from zero. Substitution of this expression for $E_r$ in the differential equation furnishes two separate relations for $K$ and $P$, with the solution

$$i^\nu K_\nu(r) = C_\nu(r) - iS_\nu(r)$$

for all points outside the particle, whereas for points inside the particle there remains the solution

$$K_\nu(r) = S_\nu(r)$$

The functions $S$ and $C$ are simple Bessel functions for which the order is half an odd integer:

$$S_\nu(r) = \sqrt{\frac{\pi r}{2}} J_{\nu+\frac{1}{2}}(r) \qquad \text{and} \qquad C_\nu(r) = (-1)^\nu \sqrt{\frac{\pi r}{2}} J_{-\nu-\frac{1}{2}}(r).$$

The equation for $P(\theta,\phi)$ is identical with the differential equation valid for the functions known as spherical surface harmonics or Laplace functions used in certain solutions of the wave equation. Since

$$\epsilon^{2\pi i n s/\lambda} = \epsilon^{i r \cos\theta} = \sum_1^\infty (2\nu + 1)i^{\nu-1}\frac{S_\nu(r)}{r^2}\Pi_\nu(\cos\theta)$$

where

$$\Pi_\nu(\cos\theta) = \frac{P_\nu(\theta,\phi)}{\cos\theta},$$

the incident plane wave also can be considered as composed of an infinite number of waves of varying amplitudes expressed by products of the same kind of Bessel functions of $r$, and Laplace functions of $\theta$ and $\phi$, for instance,

$$E_r = \sum_1^\infty (2\nu + 1)i^{\nu-1}\frac{S_\nu}{r^2}P_\nu$$

All the components have the same frequency and must not be confused with natural partial waves.

The electric and magnetic amplitudes that the incoming plane wave of unit amplitude excites along the axes of co-ordinates add themselves to the similar amplitudes, proportional to $a_\nu$ and $p_\nu$, set up by vibrations returning from the particle but involving the functions $E_\nu = C_\nu - iS_\nu$. In the interior of the particle the amplitudes are proportional to $b_\nu$ and $q_\nu$. According to the equations of continuity for the boundary surface, at the distance $\rho = a$, the following relations hold at any time for each of the $\nu$ vibrations:

$$-(2\nu + 1)S'_\nu(\alpha) + a_\nu E'_\nu(\alpha) = (-1)^\nu\alpha/\beta\, b_\nu S'_\nu(\beta)$$
$$-(2\nu + 1)S_\nu(\alpha) + a_\nu E_\nu(\alpha) = (-1)^\nu b_\nu S_\nu(\beta)$$
$$(2\nu + 1)S_\nu(\alpha) + p_\nu E_\nu(\alpha) = (-1)^\nu\alpha/\beta\, q_\nu S_\nu(\beta)$$
$$(2\nu + 1)S'_\nu(\alpha) + p_\nu E'_\nu(\alpha) = (-1)^\nu q_\nu S'_\nu(\beta)$$

Therefore the amplitudes of electrical vibrations issuing from the particle must be equal to

$$a_\nu = (2\nu + 1)(-1)^\nu\frac{\beta S'_\nu(\alpha)S_\nu(\beta) - \alpha S_\nu(\alpha)S'_\nu(\beta)}{\beta E'_\nu(\alpha)S_\nu(\beta) - \alpha E_\nu(\alpha)S'_\nu(\beta)}$$

the amplitudes of the magnetic vibrations leaving the particle are

$$p_\nu = -(2\nu + 1)(-1)^\nu\frac{\beta S_\nu(\alpha)S'_\nu(\beta) - \alpha S'_\nu(\alpha)S_\nu(\beta)}{\beta E_\nu(\alpha)S'_\nu(\beta) - \alpha E'_\nu(\alpha)S_\nu(\beta)}.$$

With the aid of these amplitudes it is possible to express the components $E_r$, $E_\theta$, and $E_\phi$ of the electric wave at any point given by the modified distance $r$, the co-latitude $\theta$, and the longitude $\phi$.

When the actual distance from which the particles are observed (or if they are too small to be seen, the effects produced by them), measures thousands

of wave-lengths, the amplitudes in the medium at the point $r$, $\theta$, $\phi$ outside the particles become

$$E_\theta = iM_\phi = -\frac{i}{r}\,\epsilon^{-u}\Sigma\left(\frac{a_\nu}{\nu(\nu+1)}\,\Pi_\nu + \frac{p_\nu}{\nu(\nu+1)}\,(\cos\theta\,\Pi_\nu - (1-\cos^2\theta)\Pi_\nu')\right)$$

$$E_\phi = -iM_\theta = -\frac{i}{r}\,\epsilon^{-u}\Sigma\left(\frac{a_\nu}{\nu(\nu+1)}\,(\cos\theta\,\Pi_\nu - \Pi_\nu'\cdot\sin^2\theta) + \frac{p_\nu}{\nu(\nu+1)}\,\Pi_\nu\right)$$

$$E_r = 0.$$

These formulas are valid on the assumption that with the electrical vibrations parallel to axis $x$, the amplitude of the plane wave of light that arrives along axis $z$ is taken as unit amplitude. In practice the directions along which the particle is observed will be so chosen that they lie either in the plane of the equator $(y, z)$, while the wave advances along $z$, and for these directions $\theta = \pi/2$, or in the plane $(x, z)$ containing the electric oscillations, and for these directions $\phi = \pm\pi/2$. The electrical component $E_\phi$ along the circles of latitude vanishes for these special values; only the component $E_\theta$ along the meridian remains. It will be designated as $E_1$ when the particle is viewed from a point in the plane $(y, z)$, and as $E_2$ when the optical effects are observed from a point lying in the plane $(x, z)$. When the electrical oscillations in the incident wave are perpendicular, instead of parallel, to axis $x$ in the plane $(x, z)$, the designations $E_1$ and $E_2$ have to be interchanged. Unpolarized light is resolved into two components, one of them parallel, the other perpendicular to axis $x$.

The intensity of the light received in a direction is proportional to the square of the amplitude. The amplitude of the incoming plane wave was assumed to be unity. If the actual intensity is integrated around the particle for the duration of one second over the entire surface of a sphere whose area is very large compared to unity, the result contains positive and negative terms. The negative quantity represents the power withdrawn by the obstacle from the wave of unit amplitude and intensity; if there is one particle per unit volume, $k$ represents therefore the power lost per unit length of path by scattering or diffraction, and at the same time the loss due to electrical convection currents excited in the particle. If there is one particle in unit volume, the total loss per unit path is equal to the real portion in the expression

$$k = \frac{-i}{2\pi}\,\frac{\lambda^2}{m^2}\Sigma\,(-1)^\nu(a_\nu - p_\nu).$$

The positive term

$$k_s = \frac{1}{2\pi}\,\frac{\lambda^2}{m^2}\sum_1^\infty\frac{|a_\nu|^2 + |p_\nu|^2}{2\nu+1}\;.$$

represents the intensity of the radiation emitted by the particle. The difference $(k - k_s)$ must be considered as the component of the radiation dissipated as heat.

## Size of Carbon Black Particles

Enormous quantities of fine carbon particles are produced in the manufacture of carbon black, an industry that has acquired considerable importance during the last 30 years (4).   The annual output amounts at present to about 250,000 tons, produced almost entirely in the United States.   The principle of manufacture is the simple method according to which, in the absence of better protection for the eyes, soot is deposited from a luminous flame on a piece of glass intended for viewing the sun or other bright source of light. The finest particles obtained on a commercial scale are produced by the combustion of natural gas in a regulated supply of air, followed by rapid cooling of the flame gases.   Thousands of flames in rows and groups impinge on the flat lower surface of a metal channel that is drawn slowly back and forth, catching the carbon particles in the rising flame before they have time to grow into very coarse grains.   For the manufacture of special types of carbon black, discs and rollers have been used on occasion as depositing surfaces.

In another method the gas is burned in large flames, the clouds of smoke are collected in water, the powder is allowed to settle, and afterwards it is filtered, pressed, and dried.   Electrostatic precipitation is also resorted to for gathering the particles.   Carbon produced by such methods is known commercially as lamp black.   The so-called thermatomic black is obtained by heating the hydrocarbon gases to temperatures at which they dissociate.   Not all available supplies of natural gas are suited to the manufacture of carbon black. Gases rich in methane but poor in ethane give a hard graphitic grade of carbon black.   Production methods in which the carbon is deposited on a moving surface, whether it be channel or roller, give the finest particles.   In any case, however, the average particles produced by any of these methods are too small to be seen under the microscope, so that a study of the light they diffract or scatter is of interest.

In one of the earliest accurate and direct determinations of the size of carbon particles Mie's theory of scattering was used and the value of 175 m$\mu$ was obtained for the diameter of the carbon grains in a luminous flame fed by amyl acetate (7).   This dimension must be considered as an average for lamp black and as an upper limit for gas black, because the size of the grains was limited only by the natural draught set up by the burner.   Studies on carbon blacks with the aid of the ultra-microscope, or the study of sedimentation, or of carbon black diaphragms, and of precipitation in an electric field, gave diameters between about 50 and 60 m$\mu$.   In a recent investigation the electron microscope was applied to the problem; in another the rate of settling in a centrifuge was measured (3, 6).   Both studies lead to the same mean value of the diameter, namely, 30 m$\mu$ for typical samples of channel black.   Despite this small size, corresponding to a mass of $2.3 \times 10^{-17}$ gm. if the specific weight is assumed to be equal to 7/4, each particle still contains about one million carbon atoms. The particles are not pure carbon, however, but contain slight traces of mineral and organic compounds.   The fact that with these small spheres the time of grinding of Portland cement is reduced and the fineness enhanced suggests

that they are solid-particles for which the optical constants obtained for arc carbons can be used (8). The study with the electron microscope led more-over to the conclusion that the preponderating form of the ultimate particles is spherical and that these fine grains may be treated as sensibly isotropic (3).

The refractive index of amorphous carbon, measured on electrodes of high purity is equal to $m = n(1 - i\kappa)$, where $n$ may be taken with sufficient accuracy as equal to 2, and $n\kappa$, the absorption index, is equal to 2/3. When a plane wave has travelled a distance $\lambda$ through a solid piece of carbon, its amplitude drops therefore to the fraction (exp.) $- 2\pi\kappa n$ or 0.015, the length $\lambda$ being measured in air. The optical properties of this substance may be considered as constant throughout the visible spectrum.
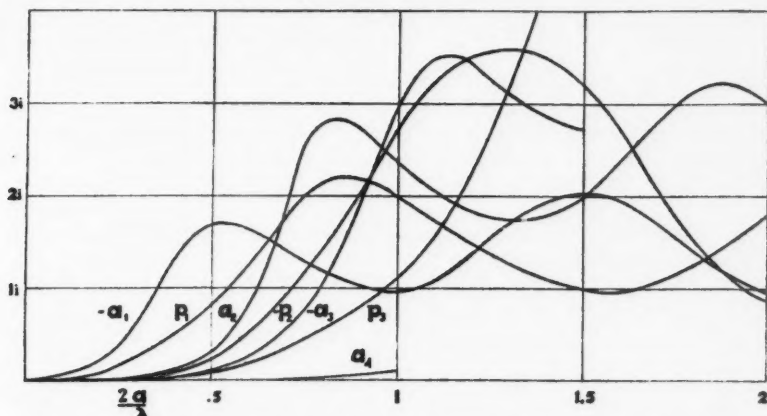


FIG. 2. *Amplitudes $a_\nu$ and $p_\nu$ of the electric and magnetic components of the oscillations issuing from the spherical obstacle and interfering in the outer medium with the oscillations of the incoming plane wave of unit amplitude.*

The absorption obtained in the presence of one carbon particle per unit volume is too small to be measured, since it is proportional to the product of $\lambda^2$ and a small number. However, as long as the number of particles per unit volume is not sufficient to cause overlapping, the coefficient of absorption $k$ of the suspension of particles is proportional to the number of particles. It may be assumed that when the concentration of the carbon grains is such that they are unable to cover 1 sq. cm. after having been collected from 1 cu. cm. and placed side by side, there is no danger of serious overlapping. With particles 200 m$\mu$ in diameter there is room for $2.5 \times 10^9$ particles per unit area; with particles 20 m$\mu$ in diameter this number increases one hundredfold. Even with the larger particles it is therefore safe to compute the absorption coefficients for small multiples of $10^9$ particles per unit volume. With concentrations greater than $10^{12}$ particles per cc., it becomes necessary to consider the finite free path of the light between particles.

The formula for the absorption coefficient may be written

$$k = -iN \frac{\lambda^2}{2\pi m_0^2} \sum_1^\infty (-1)^\nu (a_\nu - p_\nu) = -2i \frac{\pi a^2 N}{\alpha^2} \sum_1^\infty (-1)^\nu (a_\nu - p_\nu)$$

and it is valid so long as $N\pi a^2$, the total area of cross-section of the particles, is smaller than unity. On introducing the Bessel functions of half-integral order, the terms $a_\nu$ and $p_\nu$ are given by the simple formulae.

$$\frac{(-1)^\nu (2\nu+1)}{a_\nu} = -i + (-1)^\nu \frac{J_{-\nu-\frac12}(\alpha)}{J_{\nu+\frac12}(\alpha)} \frac{\dfrac{\beta}{\alpha} \dfrac{J'_{-\nu-\frac12}(\alpha)}{J_{-\nu-\frac12}(\alpha)} - \dfrac{J'_{\nu+\frac12}(\beta)}{J_{\nu+\frac12}(\beta)}}{\dfrac{\beta}{\alpha} \dfrac{J'_{\nu+\frac12}(\alpha)}{J_{\nu+\frac12}(\alpha)} - \dfrac{J'_{\nu+\frac12}(\beta)}{J_{\nu+\frac12}(\beta)}}$$

$$-\frac{(-1)^\nu (2\nu+1)}{p_\nu} = -i + (-1)^\nu \frac{J_{-\nu-\frac12}(\alpha)}{J_{\nu+\frac12}(\alpha)} \frac{\dfrac{\beta}{\alpha} \dfrac{J'_{\nu+\frac12}(\beta)}{J_{\nu+\frac12}(\beta)} - \dfrac{J'_{-\nu-\frac12}(\alpha)}{J_{-\nu-\frac12}(\alpha)}}{\dfrac{\beta}{\alpha} \dfrac{J'_{\nu+\frac12}(\beta)}{J_{\nu+\frac12}(\beta)} - \dfrac{J'_{\nu+\frac12}(\alpha)}{J_{\nu+\frac12}(\alpha)}}$$

where

$$J'_{\nu+\frac12}(\alpha) = J_{\nu-\frac12} - \frac{2\nu+1}{2\alpha} J_{\nu+\frac12}$$

$$J'_{-\nu-\frac12}(\alpha) = -J_{-\nu+\frac12} - \frac{2\nu+1}{2\alpha} J_{-\nu-\frac12}$$

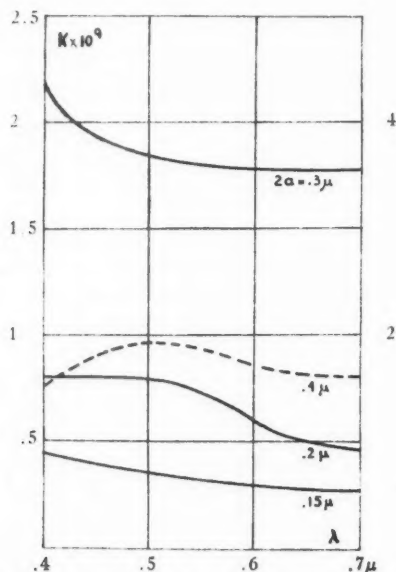Fig. 2 shows the values of the first terms $a_1$, $a_2$, and $p_1$, $p_2$ when the ratio $2a/\lambda$ increases from 0 to 2.



FIG. 3. *Coefficient of absorption for different particle sizes (radius a = 0.075 to 0.2μ) at various ratios 2a/λ. (The scale for 4 μ is on the right.)*

A glance at the expressions for $a_\nu$ and $p_\nu$ shows that they are functions of the ratio $2a/\lambda$, not of $a$ and $\lambda$ separately (1). The dimensions enter only through the product $N\pi a^2$, the total area of cross-section in unit volume, with which the sum of the differences has to be multiplied in order to obtain the coefficient of absorption. Were there no diffraction or scattering, the carbon particles would behave as simple geometrical screens, and the absorption coefficient would be proportional to $N\pi a^2$. The coefficient tends toward this value for the larger particles, but possesses higher values for small ratios $2a/\lambda$; moreover it varies markedly with the wave-length despite the fact that the optical constants of a solid block of carbon, which show no difference between wave-lengths in the visible spectrum, have been assumed to be valid. The coefficient of absorption (Fig. 3) increases toward the blue when the particles have a diameter of $0.1$ to $0.2\ \mu$, the increase amounting to more than $40\%$ between $700\ m\mu$ and $500\ m\mu$. A cloud of such particles will appear red by transmitted light, and blue in scattered light, an effect well known from the observation of columns of smoke. An opposite effect is obtained for the larger particles of $0.3$ and $0.4\ \mu$, but the percentage change is small, and the particles assume more and more the properties of the gray body represented by amorphous carbon.

## Acknowledgment

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## PHASE EQUILIBRIA IN THE TWO COMPONENT SYSTEM, ETHYLENE-PROPYLENE, IN THE CRITICAL TEMPERATURE REGION[1]

### By W. G. Schneider[2] and O. Maass[3]

### Abstract

Phase equilibria measurements have been made for a 1 : 1 ethylene-propylene system in the critical temperature region by means of an equilibrium apparatus described by Holder and Maass (3). The critical density of the system was found to be 0.230 gm. per cc. and the critical temperature $58.30° \pm 0.05°$ C. For mass-volume ratios greater than 0.230, at constant volume, the temperature of liquid disappearance was lower than 58.30° C., while for mass-volume ratios less than 0.230, the temperature of liquid disappearance was higher than 58.30°C. With stirring, the phase compositions and phase densities of the liquid and vapour phases were shown to become equal at the critical temperature, whereas in the absence of stirring the attainment of equilibrium is slow and uncertain. The results are discussed on the basis of the liquid persistence theory (5), and the vapour-liquid dispersion theory (1, 9).

### Introduction

A series of investigations in the critical temperature region has been carried out in this laboratory with one component systems, and in general the results indicated a discontinuity of property at the critical temperature (2, 3, 6, 7, 11, 15, 18, 20). This phenomenon was explained by the hypothesis of a liquid structure characterized by a regional orientation (5) which persists at the critical temperature and over a finite temperature range above the critical temperature. The present work is an attempt to study the behaviour of a two component system in the critical temperature region, and especially to determine whether a discontinuity in phase composition can be detected at the critical temperature.

### Apparatus

To study the composition of the two phases of the system in the critical temperature region, it was necessary to obtain a representative sample of each phase in such a way that the equilibrium of the system would not be disturbed. This was possible with an apparatus similar in principle to that used in this laboratory by Holder and Maass (3). A new assembly was constructed which embodied several modifications of their apparatus. Fig. 1 shows a cross-section of the main features of the apparatus. It consisted of

a central main bomb to which two small sampling bombs, *B* and *C*, were attached.    The main bomb was machined from a bar of stainless steel (18-8 composition, "Sta-brite").    This material was chosen because it was found that the phosphor-bronze bomb employed by Holder and Maass (3) was
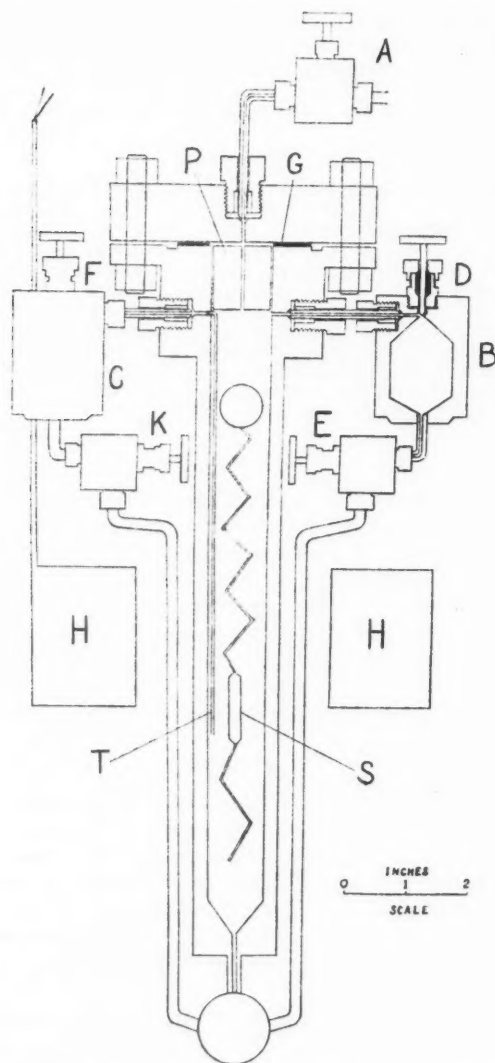


FIG. 1.    *Schematic diagram of the equilibrium bomb assembly.*

slowly attacked by mercury.    Moreover phosphor-bronze has not a sufficiently high tensile strength, and threads cut into it at the joints yielded.    The stainless steel used is non-magnetic; this made possible the use of an electromagnetic stirrer.    The depth of the main bomb was 11 in. and the inside diameter 13/16 in.; the wall thickness was $\frac{1}{4}$ in.    These dimensions allowed mercury to run out of the sampling bombs readily.    At the top of the bomb a shoulder was left to which the sampling bombs could be joined, and above this a flange $4\frac{1}{4}$ in. in diameter to which the cover could be bolted.    The cover was 1 in. thick and was fastened to the bomb by means of four $\frac{3}{8}$ in. steel bolts.    A lead gasket $G$ was held in place by two V-grooves on the seat of the bomb, and two V-shaped tongues on the cover.

The sampling bombs, $B$ and $C$, were made of cold rolled steel.    These units were the same as used by Holder and Maass (3), and consisted of a reservoir and a needle valve combined in a single body.    The sampling bombs were joined to the bottom of the main bomb by welding; this permitted the use of liquid air in charging the bomb.    The bottom or liquid sample was drawn into the sampling bomb $C$ through a fine stainless steel tube $T$, which extends approximately two-thirds of the distance down the main bomb.    The plug $P$ merely served to reduce the unavoidable dead space at this point.    Graphite and string were used for the valve packings.

The stirrer $S$ consisted of a glass-encased iron core with a sturdy glass spiral joined to each end; a bulb, about $\frac{5}{8}$ in. in diameter, at the top end steadied the stirrer in its up and down motion and set up a turbulence in the vapour phase to ensure efficient mixing.    The stirrer was operated by a solenoid $H$ enclosed in a brass case; the internal diameter of the solenoid ($3\frac{3}{4}$ in.) was sufficient to prevent any temperature gradient along the length of the tube due to heat from the solenoid.         .

The thermostat consisted of a cylindrical copper tank, fitted with two windows, and equipped with two high speed, four-blade stirrers.    A high boiling hydrocarbon oil (Marcol HX) was used as the thermostat liquid. Heating as well as regulation of the thermostat was effected by means of a single intermittent 250 watt heater placed half-way down the side of the bath. Thermocouples placed at various points in the thermostat showed no temperature gradients either in the bath itself, or around the solenoid and along the length of the equilibrium bomb.    Temperature control was good to within 0.01° C.    The thermometer used throughout was calibrated against a platinum resistance thermometer.

Ethylene and propylene were obtained from the Ohio Chemical Co.    The ethylene gas was certified 99.5% pure, and the propylene 99.8% pure.    The gases were purified by fractional distillation.    The critical properties of ethylene and propylene are summarized in Table I.

TABLE I

THE CRITICAL PROPERTIES OF ETHYLENE AND PROPYLENE

| — | $T_c$,° C. | $P_c$, atm. | $d_c$, gm./cc. | Reference |
|---|---|---|---|---|
| Ethylene | 9.2 (9.7) | 50.9 | 0.22 | (13, 16) |
| Propylene | 91.4 | 45.4 | 0.233 | (19) |

## Experimental Procedure

### 1. Preparation for an Experiment

In the equilibrium bomb 40.0 cc. of mercury was placed. The cover was then bolted on and the bomb connected to the gas reservoirs. The needle valves on the sampling bomb B were opened, while the valves of sampling bomb C were closed. The system was then evacuated. Valve D was closed, and ethylene or propylene admitted to the apparatus to a pressure of $1\frac{1}{2}$ atm., forcing mercury up through valve E and filling the reservoir B. Valve E was then closed. Sampling bomb C was filled with mercury in the same manner. When both sampling bombs were filled, enough mercury remained in the main bomb to cover the bottom. The apparatus was then again thoroughly evacuated and flushed twice with propylene or ethylene.

### 2. Filling the Equilibrium Bomb

The volume of the equilibrium bomb, when it was ready to be charged (i.e., when the sampling bombs were filled and a little mercury remained in the bottom of the bomb) was calibrated by weighing with mercury. This volume was 87.4 cc. The amounts of ethylene and propylene required to give a 1 : 1 mixture and a mass volume ratio of 0.230 were calculated and condensed into the bomb with liquid air, propylene being condensed first. The amount of each gas condensed was measured accurately by the change in pressure in a calibrated volume, both gases being measured successively from the same volume. The error in the measurement of the masses of the gases condensed into the bomb is believed to be considerably less than 0.1%.

The charged bomb was placed in the thermostat at the desired temperature, and the stirrer started. Thermostating was continued for 14 hr. or longer with continuous stirring to allow the system to come to equilibrium. The rate of stirring varied from 75 to 120 strokes per min. (a stroke including one up and down motion of the stirrer). Between these limits the final equilibrium obtained was apparently independent of the rate of stirring.

### 3. Sampling

In withdrawing the phase samples, that of the "liquid" or lower phase was taken first. Valves F and K (Fig. 1) were opened for a sufficient time for the mercury to run down into the main bomb. In the same way the vapour or upper sample was drawn into the sample bomb B by opening valves D and E.

The apparatus was removed from the thermostat and the pressure in the main bomb was released. The samples were then expanded into calibrated volumes and the pressures and temperatures recorded.

### 4. Analysis of the Samples

The samples were analysed in a low temperature still of the Podbielniak type (17). By fractionating known samples of ethylene and propylene, analysis by this method was found to be accurate to 0.3%.

## Results

### 1. Critical Temperature and Critical Density of a 1 : 1 Ethylene-Propylene Mixture

Before any measurements of the phase equilibria of the system in the critical region could be carried out, it was necessary to determine the critical temperature and the critical density of the system. This was accomplished by filling thick-walled glass bombs to various densities with the carefully purified gases and observing the temperature of meniscus disappearance as the bomb is gradually heated (0.1° C. per hour), the rate of stirring being the same as in the steel equilibrium bomb. The results of a number of measurements are summarized in Table II, and are plotted in Fig. 2. For a mass-volume ratio less than 0.230, the meniscus remained more or less stationary until the temperature was a few tenths of a degree below that of the liquid disappearance, when it gradually moved to the bottom and disappeared as the temperature was raised. On lowering the temperature again, the first traces of liquid appeared at the bottom of the bulb. The temperature of disappearance and reappearance of liquid was found to coincide to within 0.01° C.; this indicated therefore a true equilibrium, which cannot be attained without stirring. When the system was not agitated, the temperature of meniscus disappearance was somewhat indefinite, owing to the opalescence produced, and was generally about 0.2° C. higher than the equilibrium values given in Table II, whereas the temperature of liquid reappearance was about 0.3° C. lower.

TABLE II

RELATION OF THE CRITICAL TEMPERATURE TO THE MASS-VOLUME RATIO
WITH STIRRING OF THE MEDIUM

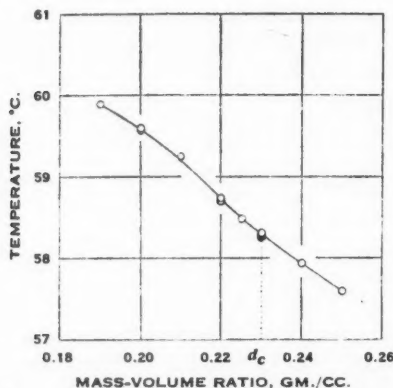| Mass-volume ratio, gm./cc. | Temperature of disappearance of liquid, ° C. | Position of meniscus disappearance | Mass-volume ratio, gm./cc. | Temperature of disappearance of liquid, ° C. | Position of meniscus disappearance |
|---|---|---|---|---|---|
| 0.190 | 59.89 | Bottom | 0.230 | 58.27 | Middle |
| 0.200 | 59.56 | " | 0.230 | 58.31 | " |
| 0.200 | 59.59 | " | 0.230 | 58.29 | " |
| 0.210 | 59.25 | " | 0.230 | 58.31 | " |
| 0.220 | 58.70 | " | 0.240 | 57.94 | Top |
| 0.220 | 58.74 | " | 0.250 | 57.59 | " |
| 0.225 | 58.48 | Below middle | | | |

Fig. 2.    *Curve showing the relation of the temperature of liquid disappearance to the mass-volume ratio in the critical temperature region for a 1 : 1 ethylene-propylene system.*

These results are in agreement with the experiments of Mason, Naldrett, and Maass (9, 13) using a shaking bomb in studying the critical behaviour of the one component systems ethylene and ethane.

For a mass-volume ratio greater than 0.230, the meniscus rose and disappeared at the top of the bulb as the temperature was raised.    For a filling of 0.230 alone the meniscus remained almost stationary until it disappeared at the middle of the bulb, and this was therefore taken as the critical density. The temperature of liquid disappearance corresponding to this density, $58.30° \pm 0.05°$ C., was taken as the critical temperature of the mixture.    It will be observed that for a two component system the true critical temperature (corresponding to the critical density as defined above) is not the maximum of the classical parabolic vapour-liquid co-existence curve, as is true for a one component system.    Fig. 2 represents one branch of this curve only, but it is obvious that the maximum of the complete vapour-liquid co-existence curve must lie at a density considerably less than the critical.    This relation was early observed by Kuenen (4).

From the results of Table II it is further evident that true critical phenomena (characterized by a meniscus disappearance at the critical temperature near the middle of the bulb) for the system under investigation will occur only over a very limited density range near the critical density.    Owing to this limited critical density range, and because it was necessary to have the meniscus disappear in the middle of the equilibrium bomb to ensure a true phase sampling near the critical temperature, the phase equilibrium measurements were confined to the critical density, 0.230 gm. per cc.

## 2. Results of Phase Equilibria Measurements in the Critical Temperature Region

Some preliminary experiments were carried out in which the medium was not stirred.    It was found however that even after 12 hr. thermostating at the highest temperature studied, $63.23°$ C., the compositions of the liquid

and vapour phases differed by about 34 mole per cent of ethylene, and the phase densities were 0.13 and 0.36 for the vapour and liquid phases, respectively. It was also found that agreement in the results was poor. It therefore appeared that without stirring the attainment of equilibrium was slow and uncertain. In all subsequent experiments the measurements were carried out with stirring in the manner described above. The period of thermostating varied from 13 to 20 hr. With the rate of stirring used, equilibrium was no doubt reached in a considerably shorter time. It was found convenient however to thermostat the equilibrium bomb overnight.

TABLE III

PHASE EQUILIBRIUM DATA OF 1 : 1 ETHYLENE-PROPYLENE SYSTEM IN THE CRITICAL TEMPERATURE REGION

| Expt. no. | Temp., ° C. | Vapour phase | | Liquid phase | |
|---|---|---|---|---|---|
| | | Density, gm./cc. | Composition, mole per cent ethylene | Density, gm./cc. | Composition, mole per cent ethylene |
| 1 | 58.68 | 0.226 | 50.3 | 0.233 | 50.0 |
| 2 | 58.43 | 0.230 | 50.1 | 0.232 | 49.9 |
| 12 | 58.38 | 0.230 | 50.4 | 0.232 | 50.1 |
| 7 | 58.34 | — | 50.2 | 0.232 | 50.2 |
| 3 | 58.28 | 0.207 | 50.7 | 0.257 | 49.4 |
| 5 | 58.12 | 0.194 | 51.6 | 0.268 | 48.8 |
| *11 | 58.14 | 0.196 | 51.3 | 0.266 | 48.9 |
| 8 | 57.67 | 0.182 | 51.8 | 0.284 | 48.2 |
| 14 | 57.67 | 0.182 | 52.2 | 0.279 | 48.1 |
| 4 | 57.00 | 0.168 | 53.0 | 0.290 | 47.5 |
| 9 | 56.04 | 0.157 | 53.4 | 0.307 | 46.7 |
| 6 | 55.84 | 0.158 | 53.6 | 0.306 | 46.8 |
| 13 | 55.02 | 0.151 | 54.2 | 0.313 | 46.3 |
| 10 | 54.13 | 0.142 | 54.5 | 0.321 | 45.9 |

*Temperature raised to 58.70° C. and kept constant for 12 hr., then lowered to 58.14° C. and thermostating continued for 13 hr.*

The results of the phase equilibrium measurements are summarized in Table III. The first column gives an indication of the order in which the runs were carried out. The phase densities were calculated from the volume, pressure, temperature, and composition of the expanded samples, and the volume of the sample bombs. The volumes of the sample bombs were calibrated by weighing with mercury, and were 15.43 and 15.40 cc. for the vapour and liquid sample bombs, respectively. It is difficult to estimate the error of the phase densities obtained in this way. The detailed manipulation of the phase samples concerned limits the accuracy with which these values can be determined. Another difficulty was the occasional failure of the mercury to drain out of the sampling bombs completely when the phase samples were being withdrawn. However the regularity of the results in Table III seems to indicate that the error due to this cause is not as great as might be expected. Taken as a whole, the calculated densities are considered

to represent fairly good approximations of the relative phase densities, rather than absolute values of the phase densities.

The calculated phase densities are plotted in Fig. 3 and the phase compositions in Fig. 4. The density-temperature curve exhibits a very flat crest at the critical temperature, which, considering the limits of experimental error, could be drawn as a horizontal line. In this respect the curve is very similar to the density-temperature curve obtained by Mason, Naldrett, and Maass (9, 13) in studying the critical behaviour in a one component system using a shaking bomb.
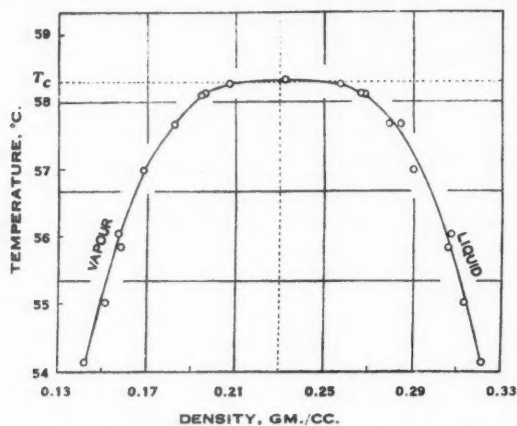


FIG. 3. Plot of the density of the co-existing vapour and liquid phases in the critical temperature region.
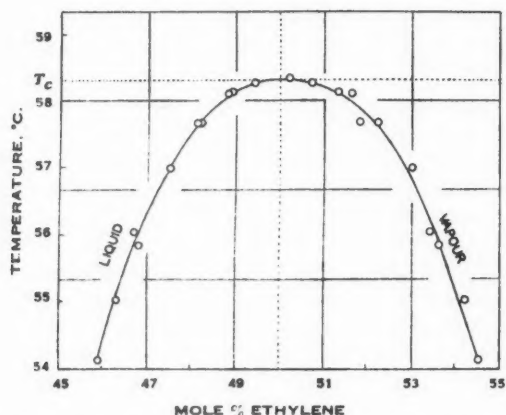


FIG. 4. Curve showing the phase compositions of the co-existing vapour and liquid phases plotted against temperature in the critical temperature region.

## Discussion

The phase compositions obtained at each temperature are considered to represent true equilibrium conditions. The time of thermostating as well as the rate of stirring were ample to allow equilibrium to be attained. With the same rate of stirring in the glass bombs, the liquid phase was found to appear and disappear within a range of $0.01°$ C. at the critical temperature; this indicated a rapid establishment of equilibrium under these conditions. Finally, it has been demonstrated (Expt. no. 11, Table III) that the same equilibrium state is obtained when the system is first heated above the critical temperature, as when it is brought from a lower temperature and thermostated at the chosen temperature. The equilibrium is thus reversible with respect to temperature.

Although the meniscus behaviour in the equilibrium bomb could not be observed directly, it was possible to obtain fairly convincing evidence that a liquid phase was present in the equilibrium bomb at a temperature as high as $58.28°$ C. by the sound of the glass stirrer moving up and down in the metal bomb. In the absence of liquid (i.e., above the critical temperature) the noise of the stirrer moving up under the magnetic field and striking the bottom when the field was off was somewhat muffled, whereas in the presence of liquid the noise was particularly audible. By holding the ear close to the top metal support of the bomb a characteristic "swishing" of the liquid could be heard while it was being stirred.

The results of Table III indicate that the experimentally measured compositions as well as the densities of the vapour and liquid phases become uniform at the critical temperature. In this respect the results are in apparent disagreement with those of Winkler and Maass (20) who found a density discontinuity to persist in a one component system at the critical temperature when the medium was stirred. The stirring in the present work however is believed to be much more vigorous and efficient, and might be expected to favour a mutual dispersion of the liquid and vapour phases near the critical temperature, so that a density discontinuity is not detectable. Experimental evidence of a vapour-liquid dispersion at the critical temperature has been obtained by several investigators in this laboratory (1, 8, 9, 10, 13, 14). It was postulated that a liquid structure persists at the critical temperature, and since the surface tension of the liquid becomes zero at this temperature (14), the liquid phase will become dispersed, partially or completely with the vapour phase, depending on the degree of stirring or agitation. This hypothesis readily explains the relatively flat portion of the phase-density–temperature curve (Fig. 3) at the critical temperature, where in the presence of stirring a rapid mutual dispersion of the vapour molecules and liquid groups may be expected, causing the measured phase densities to become rapidly equalized. It may be argued that a similar flat portion at the critical temperature should occur in the composition-temperature curve (Fig. 4) as a result of the mutual dispersion of the persistent liquid and vapour phases, which, corresponding to the unequal phase densities just below the critical temperature, may differ

appreciably in composition at the critical temperature.    To explain the actual curve obtained, the mutual solubility of the two components at the critical temperature must be considered to be either complete, or to be nearly complete and the present method to be incapable of detecting the exact behaviour. In the light of experimental evidence already accumulated on the critical temperature phenomena the present results can be most conveniently interpreted by supposing liquid groups, containing on the average an equal number of molecules of each component, to persist at the critical temperature, and to become mutually dispersed with vapour molecules, the dispersion being complete as a result of stirring of the system.    While it is true that the results could, on the other hand, be explained simply by assuming the principle of continuity of state at the critical temperature, an exceedingly rapid change of phase density with temperature at the critical point would have to be postulated to explain the density-temperature curve.    Accurate density measurements in a one component system in the absence of stirring (6, 11, 18, 20) have shown however that the change of phase density with temperature at the critical temperature is not as rapid as demanded by the theory of continuity of state, but that the change is much more gradual, corresponding to a gradual breaking-up of liquid structure which was found to persist over a finite temperature interval above the critical temperature.

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# THE DEVELOPMENT OF A PRESERVATIVE FOR GILL NETS[1],[2]

By G. Cave-Browne-Cave[3] and R. H. Clark[4]

## Abstract

In a search for an adequate preservative for gill nets many attempts were made to synthesize a plastic in the fibres of the twine. The resulting strands in no case possessed such requisite properties as sufficient flexibility and wearing qualities. Strands, treated with a solution of chlorinated pale crepe rubber, to which a plasticizer, dibutyl phthalate, and a bactericide were added, were found, by tensile strength measurements, to prolong the life of the twine in the sea. The strands had the necessary degree of flexibility, and their wearing quality was improved greatly.

Tests made by commercial fishermen on sections of net, treated according to the formula recommended, confirm in large measure the laboratory and sea immersion experiments. They report, among other findings, that the net was easier to handle, remained clean, caught an equal catch of fish as the untreated sections, and that the knots did not slip. The strength of the treated net after a summer's fishing, the fishermen found, was only slightly greater than that of the untreated net. This result was not at all in accord with the laboratory tensile strength measurements made on twine after several weeks of sea immersion. An examination of the knots revealed that this difference is due undoubtedly to the fact that the preservative did not penetrate sufficiently into the knots. Nets are now being manufactured from the treated twine; this is expected to overcome the difficulty and increase considerably the life of the net under fishing conditions.

## Introduction

The need for a satisfactory gill net preservative has existed since this method of fishing began. The need is world-wide. Carter and Charnley (1) have written as follows:—

". . . . In British Columbia alone during 1933 the value of gear in use was over $1,625,000, representing about 14% of the total value of the fish landed in the province for that year. The annual depreciation of some types of gear is very considerable, particularly in the case of salmon gill nets. In certain localities such nets costing from $100 to $150 apiece often last for only 4 to 8 weeks during a fishing season, although some serve for a season of 8 to 10 weeks' duration, and even for a part of the next season. In other localities an average of two seasons' use is obtained."

The present war has markedly aggravated the need, so that the present paper seems timely.

### Causes of Rotting of Nets in Sea Water

Bacterial action appears to be the dominant cause (2, 3, 4). That bactericides such as copper sulphate, copper oleate, and copper naphthenate are

widely used net preservatives supports the above statement. Mechanical wear on a net during fishing operations reduces the life of the net, and it is of special importance in that if a method of materially retarding bacterial action can be found, mechanical wear may then determine the life of the net. Both oxidation of the cellulose and the effect of sunlight on the cellulose contribute to the deterioration of the net. They are, however, of less importance than bacterial action.

*Desirable Properties of a Preservative and of a Treated Net*

The preservative itself should be either transparent or of a colour acceptable to fishermen. It must be easy to apply to the net. The weight of the net should not be unduly increased by the application of a preservative. In the net, bacterial action should be materially retarded; the treated net should have greater resistance to mechanical wear than the untreated net; oxidation of the cellulose should be retarded; and the harmful effect of sunlight should be minimized. Moreover, the knots of the treated net should not slip under tension before breakage occurs; the treated net must have the desired degree of flexibility. The net should be easy to handle. Finally, it must catch fish, a property not always possessed by nets treated with certain preservatives.

No commercially available preservative appears to possess, or to produce in a net, to a marked degree all these desired properties. Here, on the Pacific Coast, copper sulphate, linseed oil, and copper naphthenate are in constant use, but almost all Pacific Coast fishermen are still seeking an adequate preservative. With this need in mind the Department of Chemistry of the University of British Columbia instituted several years ago a research the object of which was to find such a gill net preservative. The problem was attacked from an angle heretofore neglected, viz.: to coat the fibres of the net twine with a plastic. Tyner and Fisher (6) experimented with several of the new plastic ingredients, synthesizing the plastic actually in the fibres of the net twine. They found that in almost all cases a net so treated was too stiff to use, but that chlorinated rubber offered promise owing to the flexibility of the treated net. The present paper records the results of a research whose object was a thorough investigation of chlorinated rubber as a preservative for gill nets.

## Experimental Methods

Linen gill net twine (5/40), from which most good nets are woven, was used exclusively. For brevity the word "strands" will be used in place of the phrase "length of twine".

*Method of Applying Preservative*

Chlorinated rubber was dissolved in benzene and a plasticizer added. Strands were soaked in this solution for a definite period of time then hung up to dry for one week, after which they were ready for the various tests.

*Methods of Determining the Value of a Preservative*

The rate at which the tensile strength of a treated strand decreases while immersed in the sea is a useful index of the value of the preservative. In this work the chief method of evaluating a preservative consisted in immersing treated strands in sea water (Coal Harbour, Vancouver) and measuring the tensile strengths of the treated strands after various immersion periods. Six-foot lengths of treated strands were suspended in sea water from a floating plank.

*Tensile Strength Measurements*

By tensile strength in this paper is meant the force in pounds necessary to break the strand, the force being increased slowly and steadily to the breaking point of the strand. Unless stated otherwise, all strands were broken, while wet, after being soaked for at least 12 hr. in water. The tensile strength was measured on a standard instrument made by Henry L. Scott and Company, the drums around which the strand was wound being 9 in. apart.

*Wearing Quality Measurements*

Taylor and Wells (5) tried various materials against which to test the wearing quality of treated strands, e.g., wood, iron, glass, and hard rubber. The most satisfactory method was to rub the strand against itself at an acute
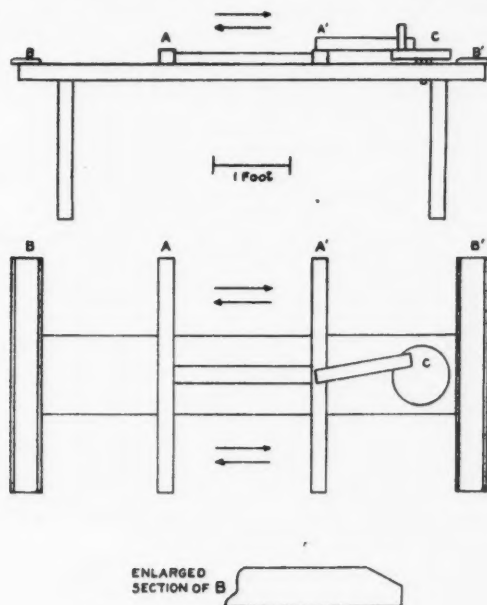


FIG. 1.   *Wearing quality apparatus.*

angle and under tension. In the present investigation it was found that a rubbing surface of bevelled glass plate provided sufficiently significant results to warrant its use. Fig. 1 illustrates the design of the instrument used. Twelve treated strands were tied to cross-pieces $A$ and $A'$ and suspended over the bevelled glass plates $B$ and $B'$. To the free end of each strand was tied a 500 gm. weight. Wheel $C$ was turned by hand at a rate of one revolution per second, causing cross-pieces $A$ and $A'$ to move in approximately simple harmonic motion, in the direction of the arrows. The strands thus wore against the glass edges. The number of revolutions of wheel $C$ was noted each time a strand broke. The wearing quality of a strand was defined as the number of revolutions of wheel $C$ necessary to cause the strand to break through wear. An average of 48 measurements was taken as the wearing quality of a strand.

### Flexibility Measurements

Tyner and Fisher (6) used no apparatus for their flexibility estimations. Taylor and Wells (5) devised an instrument by means of which a quantitative determination of flexibility may be made. Their method consists in measuring the energy dissipated when the strand bends through a definite angle. One end of the strand is attached to the end of a brass plummet. The other is held rigid. This, then, constitutes a pendulum. A definite initial phase is specified, and the number of oscillations to reduce the angle of the initial phase to one-half is taken as a measure of the flexibility. Such a method has, obviously, disadvantages. These are recorded by Taylor and Wells (5), who correct for the errors. Probably the greatest disadvantage is the large number of measurements that must be averaged in order to obtain a figure of significance.

To enable a significant measure of the flexibility of a strand to be made with as few measurements as possible, a new instrument was devised by the authors (Fig. 2).

Procedures for the operation of the flexibility instrument: One of several can be used, the choice being dependent on the time available and on the accuracy required. Below is given the procedure worked out and adopted in this investigation.

A strand was selected for a preliminary test. Ten grams was added to each scale pan. To one pan a weight ($W_2$) was added, the weight being such as to cause the pan to fall approximately 3 cm. in 25 sec. Next was selected a weight ($W_1$) necessary to cause the pan to fall approximately 3 cm. in 10 sec. Finally, a weight ($W_3$) necessary to cause the pan to fall approximately 3 cm. in 40 sec. was selected. These preliminary tests gave the weights $W_1$, $W_2$, and $W_3$, to be used in the actual determination. The procedure used in the actual determination follows:—

A new strand was selected and 10 gm. added to each pan. To one pan was added, in addition, $W_1$ gm. The length of strand chosen was such that when one pan was near the pulleys, the other almost touched the base of the
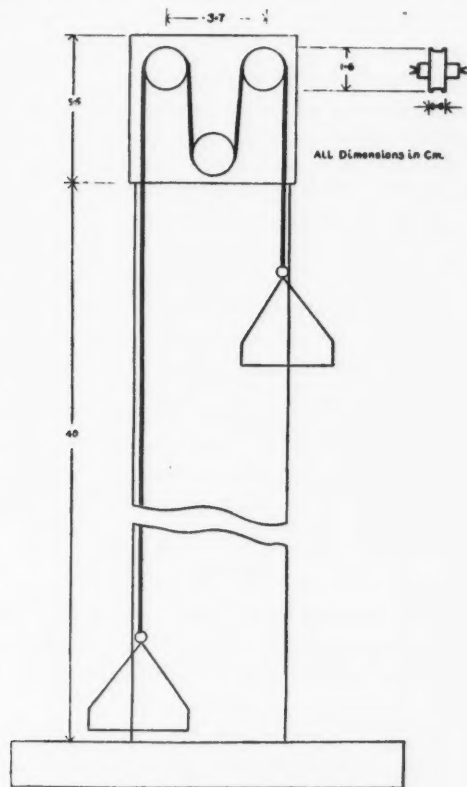
Fɪɢ. 2.   *Flexibility instrument.*

instrument.   The pans were kept from moving by a slight pressure of the finger on one pulley.   The finger was now released, allowing the pans to accelerate, and the stopwatch was started.   The pan was allowed to fall exactly 3 cm., the watch was stopped, and coincidently the pan stopped by pressing against the pulley.   The time for a 3 cm. fall was recorded ($T_1$ sec.).   The above procedure was repeated exactly, using $W_2$ gm. instead of $W_1$, and the time for a 3 cm. fall was recorded ($T_2$).   The above procedure was repeated exactly, using $W_3$ gm. instead of $W_2$, and again the time for a 3 cm. fall was recorded ($T_3$).   By this time, 9 cm. of strand had been used. Thus, there were three sets of values, namely, ($W_1$, $T_1$), ($W_2$, $T_2$), and ($W_3$, $T_3$). Weight $W_3$ now rested on the scale pan; it was replaced by $W_1$ and the entire procedure given above was duplicated.   This gave three more sets of values ($W_1$, $T_1$), ($W_2$, $T_2$), and ($W_3$, $T_3$).   The above procedure was used over and over again using new samples of strand when necessary, until 10 sets of values of ($W_1$, $T_1$), 10 of ($W_2$, $T_2$), and 10 of ($W_3$, $T_3$) were obtained.   $W$ was

then plotted against $T$. From this graph there was read off the value of $W$ corresponding to $T = 25$ sec. This interpolated value of $W$ was arbitrarily defined to be the average flexibility of the strand.

The merits of the above described apparatus are obvious. A fairly large sample can be used for measurement. Moreover, a given length of strand is bent only six times. This virtually eliminates the error likely to be caused by a variation of flexibility with the number of times the strand is bent.

### Preparation of Chlorinated Rubbers

The gum chicle, gutta percha, or pale crepe was dissolved in carbon tetrachloride. The pale crepe was first depolymerized by heating in air at 90° C. for four hours, and disaggregated with a high-speed stirrer during solution. Chlorine gas was passed through the continuously stirred solution for a definite length of time and at a definite temperature. The chlorinated rubber was then separated from the carbon tetrachloride by steam distillation. Steam was passed into the flask containing the product until, after frequently changing the condensed water in the flask, this water gave a pH reading of 5.5 or higher. The product was then crushed and dried. Some products containing a small amount of chlorine were somewhat elastic; those containing a large amount were fibrous.

## Results

### Effect of Solvent on Tensile Strength of Twine

Preliminary experiments showed that benzene, toluene, and xylene had no effect on the tensile strengths of strands immersed for six hours in each of these solvents.

### Relative Preservation Qualities of Various Chlorinated Rubbers

Fifteen different chlorinated rubbers were prepared from gum chicle, gutta percha, and pale crepe, by chlorinating solutions of these for various lengths of time and at various temperatures. In addition to these products, three samples of a commercially available chlorinated rubber, "Parlon", were secured from the manufacturers, the Hercules Powder Company, Incorporated, Wilmington, Delaware, U.S.A. These samples were of viscosity types 6, 8, and 20 centipoises. Benzene solutions (20%) of each of these 18 products were prepared, dibutyl phthalate being added as a plasticizer in such concentrations as to produce treated strands of the same degree of flexibility. Sea immersion tests over a period of four weeks showed that whereas all strands treated with chlorinated gum chicle and chlorinated gutta percha were almost completely rotted after four weeks' immersion, the strands treated with chlorinated pale crepe and those treated with Parlon still had average tensile strengths of about 20 lb. Further, Parlon was as effective a preservative as the best of the chlorinated pale crepe products, but not more so. Therefore, it was concluded that Parlon was the most suitable product for commercial use, and it was used exclusively in all later measurements.

## Extent of Knot Slippage

It was important to be sure that the treatment of a net with a solution containing Parlon produced no tendency for the knots to slip. A number of benzene solutions of Parlon plus dibutyl phthalate were prepared in which the concentrations of both Parlon and dibutyl phthalate were varied. Tests were made on the water-soaked treated sections of net. It was found that there is no knot slippage in nets treated with those preservative solutions that would be of practical use. Slippage occurred only when the concentration of plasticizer became so great that the nets would be useless owing to stickiness.

TABLE I

EFFECT OF VARIOUS PLASTICIZERS

In each experiment a solution of 20 gm. of Parlon (15 centipoises) was dissolved in 100 gm. of benzene, and the amount of plasticizer noted in Column 2 was added

| Plasticizer | Ml. of plasticizer | Tensile strength, lb. (broken wet) | | |
|---|---|---|---|---|
| | | Before immersion in sea | Immersed in sea 4 weeks (March) | Immersed in sea 7 weeks (March–April) |
| Santiciser M 17 | 11.4 | | 24.9 | 0.0 |
| | 14.0 | | 40.8 | 15.0 |
| | 16.5 | | 28.4 | 5.0 |
| Dow No. 5 | 11.4 | | 19.3 | 0.0 |
| | 14.0 | | 31.5 | 5.0 |
| | 16.5 | | 30.1 | 5.0 |
| | 19.0 | | 37.1 | 17.3 |
| | 21.5 | | 39.7 | 17.2 |
| | 24.1 | | 27.7 | 5.0 |
| Aroclor No. 1242 | 7.6 | 59.1 | 28.9 | 25.7 |
| | 10.1 | 58.6 | Lost | 30.6 |
| | 14.0 | 57.7 | 39.7 | 32.3 |
| | 19.0 | 58.1 | 46.0 | 28.1 |
| | 21.5 | 55.6 | 36.1 | 23.3 |
| | 24.1 | 52.6 | 35.0 | 20.0 |
| Tricresyl phosphate | 5.1 | 8.0 | 8.0 | 0.0 |
| | 10.1 | 17.0 | 17.0 | 5.0 |
| | 12.7 | 24.1 | 17.0 | 5.0 |
| | 15.2 | 37.6 | 37.6 | 5.0 |
| | 17.7 | 19.8 | 19.8 | 4.0 |
| | 20.3 | 10.7 | 10.7 | 0.0 |
| n-butyl stearate | 5.1 | | 8.7 | 0.0 |
| | 7.6 | | 16.3 | 0.0 |
| | 10.1 | | 16.6 | 0.0 |
| | 11.4 | | 19.0 | 0.0 |
| | 12.7 | | 14.0 | 0.0 |
| Dibutyl phthalate | 8.9 | 59.1 | 41.0 | 27.6 |
| | 10.1 | 57.2 | 45.0 | 36.0 |
| | 11.4 | 58.3 | 50.6 | 45.1 |
| | 12.7 | 55.9 | 39.1 | 33.7 |
| | 13.9 | 52.7 | 32.1 | 30.2 |
| | 15.2 | 49.3 | 30.8 | 11.5 |
| Untreated strand | | 52.0 | 0.0 | |

*Dibutyl phthalate was found to be the best plasticizer for this particular purpose.*

*Effect of the Plasticizer on the Preservative Properties of the Parlon Film*

In order to treat a net so that it has, after treatment, the requisite degree of flexibility, it is necessary to incorporate a plasticizer with the Parlon. Preliminary work showed that not only does the flexibility of a treated net vary with the ratio of plasticizer to Parlon, but that the life of the treated net in the sea is also a function of this ratio. An investigation was therefore undertaken to determine both the best plasticizer to use and the best ratio of plasticizer to Parlon.

Many plasticizers were investigated, including several commercial products sold under trade names. In Table I are given the results obtained with a few of the plasticizers tried in this work.

In Fig. 3 the concentration of dibutyl phthalate is plotted against the average tensile strengths of treated strands after four and after seven weeks' immersion in the sea. The data are taken from Table I. It is clear from this graph that there is an optimum concentration of dibutyl phthalate, namely about 11.5 ml. per 100 gm. of benzene in which 20 gm. of Parlon are dissolved. By optimum concentration is meant that concentration producing greatest longevity of strands in the sea. Further, all plasticizers investigated exhibited optimum concentrations. The reason for this optimum concentration was not investigated, but a possible explanation is that if the concentration of plasticizer falls below the optimum, the Parlon film shrinks and cracks, owing to its inelasticity, while, if the concentration of plasticizer is greater than the optimum, the porosity of the film may increase.
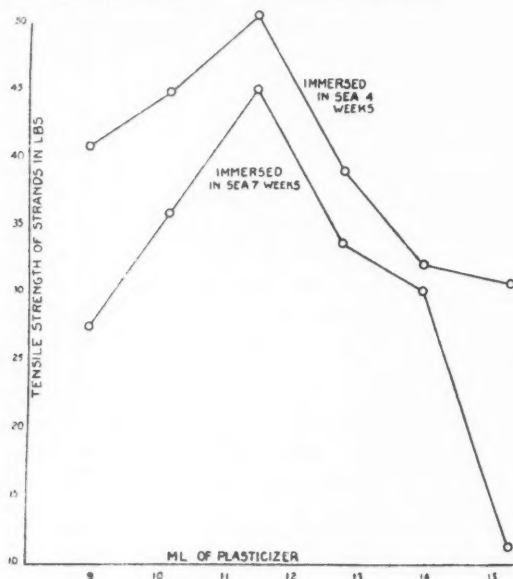


Fig. 3

*Further Investigation of Dibutyl Phthalate as Plasticizer*

Parlon is manufactured in several viscosity types. For example, viscosity type 10 centipoises means that a 20% solution in toluol at 25° C. has a viscosity of 10 centipoises. Viscosity types up to 20 centipoises were found to give solutions of viscosities low enough to be of use as gill net preservatives. Tests were therefore made to find if one viscosity type was superior to another. Since the linear density of a treated strand, and hence the film thickness, increases as the viscosity of the Parlon solution increases, the concentrations in benzene of the two types of Parlon used were not made the same, but were so chosen that the linear densities of the strands treated with the two types of Parlon were as nearly the same as possible. The results are given in Table II.

TABLE II

EFFECT OF VISCOSITY TYPE OF PARLON

| Viscosity type Parlon, centipoises | Grams of Parlon per 100 gm. of benzene | Ml. of dibutyl phthalate per 100 gm. of benzene | Linear density of treated strand, gm. per metre | Tensile strength, lb. (broken wet) | |
|---|---|---|---|---|---|
| | | | | Immersed in sea 3 weeks (April) | Immersed in sea 7 weeks (April–May) |
| 7 | 20.0 | 8.0 | 0.66 | 30.8 | 5.0 |
| 7 | 20.0 | 11.0 | 0.66 | 39.3 | 18.4 |
| 7 | 20.0 | 13.0 | 0.66 | 38.8 | 18.0 |
| 7 | 20.0 | 14.0 | 0.66 | 37.2 | 18.1 |
| 7 | 20.0 | 16.0 | 0.66 | 28.0 | 15.7 |
| 13 | 19.8 | 8.0 | 0.65 | 35.5 | 5.0 |
| 13 | 19.8 | 11.0 | 0.65 | 46.3 | 28.4 |
| 13 | 19.8 | 12.9 | 0.65 | 44.2 | 26.2 |
| 13 | 19.8 | 14.0 | 0.65 | 35.5 | 23.1 |
| 13 | 19.8 | 16.0 | 0.65 | 33.1 | 20.6 |
| Untreated strand | | | 0.44 | 0.0 | |

In Fig. 4, concentration of plasticizer is plotted against average tensile strength of treated strands after seven weeks' immersion. The data are taken from Table II.

From the figure it is clear that 13 centipoises type Parlon is superior to 7 centipoises type. Further, from this, and additional data not given, for 7 centipoises type Parlon the optimum concentration of dibutyl phthalate is 11.5 ml. per 100 gm. of benzene containing 20 gm. of Parlon, while for 13 centipoises type Parlon the optimum concentration of dibutyl phthalate is 11.1 ml. per 100 gm. of benzene containing 19.8 gm. of Parlon. It is interesting to note that the optimum concentration of dibutyl phthalate is in agreement with that recorded in Table I.

*Effect of the Length of Time of Immersion in Parlon Solution on the Life of the Treated Strand in the Sea*

Strands were soaked in Parlon solutions (20 gm. of Parlon, 11.5 ml. dibutyl phthalate, 100 gm. of benzene) for periods of time ranging from two minutes to six hours. Both 7 and 13 centipoises types Parlon were used. Sea immersion
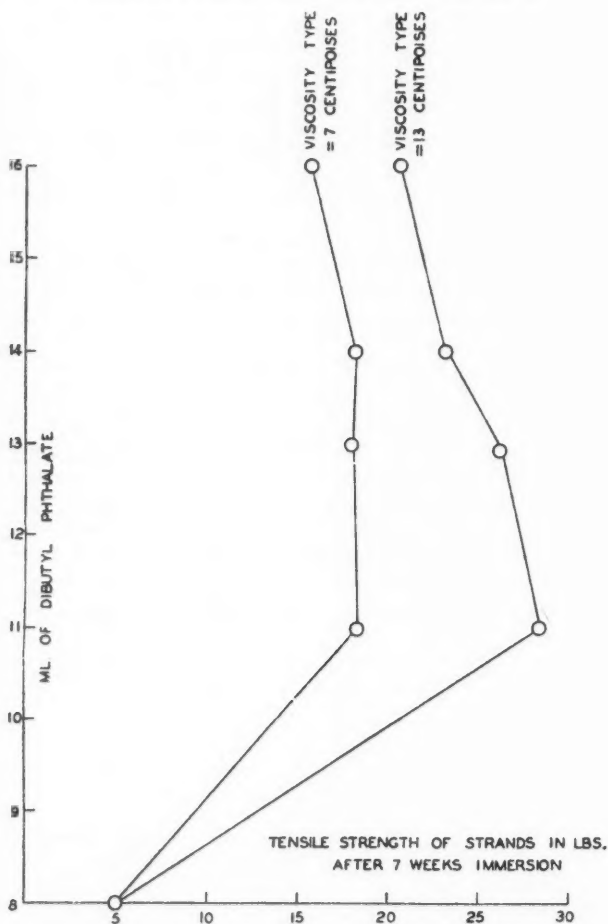
FIG. 4

tests showed that time of immersion of strand in impregnating solution has no perceptible effect on the life of the treated strand in the sea, strands soaked for two minutes in Parlon solution being as strong after seven weeks' sea immersion as those soaked for six hours. Further, this conclusion is valid for both 7 and 13 centipoises types Parlon. These data are given in Table III.

It should be noted that the above conclusion holds for twine, and not necessarily for nets. It is probable that the life of the net in the sea is a function of length of time of immersion in impregnating solution, since in a net there are knots to be impregnated.

TABLE III

EFFECT OF TIME OF IMMERSION IN PARLON SOLUTIONS

| Viscosity type Parlon, centipoises | Grams of Parlon per 100 gm. of benzene | Ml. of dibutyl phthalate per 100 gm. of benzene | Time of immersion of strand in Parlon solution | Tensile strength, lb. (broken wet) | |
|---|---|---|---|---|---|
| | | | | Immersed in sea 3 weeks (April) | Immersed in sea 7 weeks (April–May) |
| 7 | 20.0 | 13.0 | 2 min. | 40.6 | 21.4 |
| 7 | 20.0 | 13.0 | 10 min. | 40.0 | Lost |
| 7 | 20.0 | 13.0 | 30 min. | 38.3 | 17.7 |
| 7 | 20.0 | 13.0 | 2 hr. | 38.1 | 16.7 |
| 7 | 20.0 | 13.0 | 6 hr. | 37.6 | 18.7 |
| 13 | 19.8 | 12.9 | 2 min. | 45.8 | 31.3 |
| 13 | 19.8 | 12.9 | 10 min. | 44.0 | 26.2 |
| 13 | 19.8 | 12.9 | 30 min. | 43.4 | 26.5 |
| 13 | 19.8 | 12.9 | 2 hr. | 41.6 | 18.8 |
| 13 | 19.8 | 12.9 | 6 hr. | 45.4 | 29.2 |

*Effect of Concentration of Parlon Solutions on the Life of the Strand in the Sea*

Impregnating solutions consisted of mixtures of Parlon, dibutyl phthalate, and benzene. Two viscosity types, 7 and 13 centipoises, of Parlon were used. In all impregnating solutions listed in Table IV, the ratio of Parlon to dibutyl phthalate was constant.

TABLE IV

EFFECT OF CONCENTRATION OF PARLON SOLUTIONS

| Viscosity type Parlon, centipoises | Grams of Parlon per 100 gm. of benzene | Ml. of dibutyl phthalate per 100 gm. of benzene | Linear density of treated strands, gm. per metre | Tensile strength, lb. (broken wet) | |
|---|---|---|---|---|---|
| | | | | Immersed in sea 3 weeks (April) | Immersed in sea 7 weeks (April–May) |
| 7 | 10 | 6.5 | 0.55 | 29.1 | 0.0 |
| 7 | 15 | 9.8 | 0.59 | 32.1 | 18.1 |
| 7 | 20 | 13.0 | 0.66 | 37.9 | 24.0 |
| 7 | 25 | 16.3 | 0.74 | 39.9 | 31.0 |
| 7 | 30 | 19.5 | 0.84 | 46.5 | 32.0 |
| 13 | 8 | 5.2 | 0.46 | 27.4 | 0.0 |
| 13 | 14 | 9.2 | 0.59 | 35.1 | 25.5 |
| 13 | 19 | 12.4 | 0.62 | 44.1 | 32.5 |
| 13 | 24 | 15.7 | 0.67 | 46.1 | 40.2 |
| 13 | 28 | 18.3 | 0.80 | 45.4 | 39.2 |
| Untreated strand | | | 0.44 | 0.0 | |

In order to evaluate the results of Table IV, linear density was plotted against tensile strength of strand after sea immersion (Fig. 5).

Fig. 5 shows that over the entire range of linear densities used, 13 centipoises type Parlon is superior to the 7 centipoises type. The two types must of course be compared at the same linear density.

Fig. 5 is of considerable value when it is wished to decide what concentration of Parlon to use. This choice of concentration of Parlon solution cannot, however, be decided solely from Fig. 5. Factors such as cost and ease of penetration of the Parlon solution into the knots of a net must also be considered.
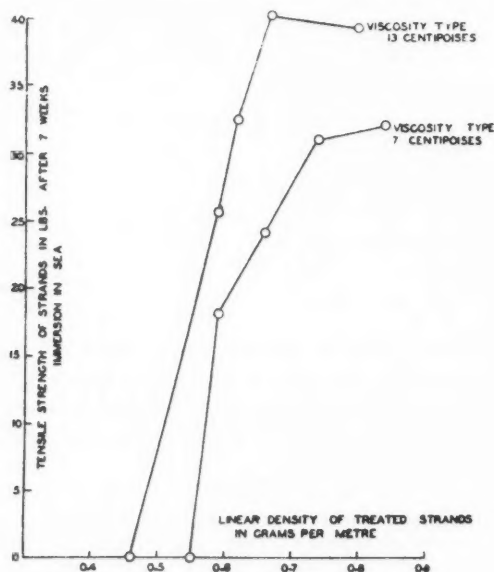


FIG. 5

*Effect of Impregnating Strands with Bactericides*

Since bacterial action is usually the most destructive force acting on gill nets immersed in the sea, it seemed natural that impregnation of the strands with a bactericide, followed by a coating of Parlon, should prove more effective in preventing rotting in the sea than a coating of Parlon alone. Further, the Parlon coating should retard the rate of washing away of the bactericide.

In most cases the strands were soaked for 30 min. in an aqueous solution of a toxic salt, dried, then soaked in a Parlon solution having the following composition: 20 gm. of 16 centipoises Parlon, 11.4 ml. of dibutyl phthalate, 100 gm. of benzene. In a few cases the toxic salt was dissolved in the Parlon solution.

The following bactericides were tried in various concentrations; silver nitrate, silver chloride, silver ammonium chloride, copper sulphate, mercuric chloride, mercurous chloride, silver sulphide, colloidal silver, mercurous sulphide, copper naphthenate, and silver naphthenate. Results of sea immersion tests on strands treated with some of the above-named salts are recorded in Table V.

## TABLE V

### EFFECT OF BACTERICIDES

All strands coated with Parlon except where noted

| Description of toxic salt treatment ($N$ = normality of solution) | Tensile strength, lb. (broken wet) | | |
|---|---|---|---|
| | Before immersion in sea | Immersed in sea 5 weeks (Jan.–Feb.) | Immersed in sea 10 weeks (Jan.–Feb.–Mar.) |
| 0.01 $N$ silver nitrate | 55.8 | 42.7 | 35.3 |
| 0.1 $N$ copper sulphate | 56.3 | 40.8 | 21.9 |
| 1.0 $N$ copper sulphate | 54.1 | 51.5 | 21.6 |
| 0.01 $N$ mercuric chloride | 54.6 | 47.7 | 37.2 |
| 0.01 $N$ silver nitrate, silver precipitated by tannin solution | 51.4 | 56.7 | 49.2 |
| 10% copper naphthenate in benzene No Parlon coating | 51.7 | 5.0 | 0.0 |
| 30% copper napthenate in benzene No Parlon coating | 55.0 | 24.0 | 0.0 |
| 10% copper naphthenate | 54.8 | 57.6 | 45.5 |
| 1% copper naphthenate in Parlon solution | 56.3 | 56.1 | 54.8 |
| 10% copper naphthenate in Parlon solution | 57.0 | 53.4 | 38.4 |
| 1% silver naphthenate in Parlon solution | 55.2 | 57.0 | 50.1 |
| Parlon coating only.  No toxic salt | 58.8 | 48.4 | 29.2 |
| Untreated strand | 51.9 | 0.0 | |

Several important conclusions can be drawn from Table V. First, treatment of strands with copper sulphate solution followed by a Parlon coating gives less effective preservation than a Parlon coating alone. The reason is probably that hydrolysis of copper sulphate occurs, and the acid formed attacks the cellulose. Second, all preservative treatments given in the table are more effective than a 30 or a 10% benzene solution of copper naphthenate with no Parlon coating. This result indicates that copper naphthenate is not as effective a preservative as its wide use indicates. It should be noted, however, that these results were obtained with twine and not with nets. Third, the most effective preservative found was a solution of 1 gm. of copper naphthenate, 20 gm. of 13 centipoises Parlon, 11.4 ml. of dibutyl phthalate in 100 gm. of benzene. Strands treated with this preservative underwent virtually no change in tensile strength after 10 weeks' sea immersion. Further, no fading of the green colour of the film could be observed. The fact that 1% of copper naphthenate in Parlon solution proved a better preservative than 10% copper naphthenate in Parlon, is interesting. The reason may be that with the higher copper naphthenate concentration some of the salt washed out of the Parlon film, leaving pores.

Some of the results given in Table V are plotted in Fig. 6. This graph illustrates in a striking way the effectiveness of the preservative consisting of 1 gm. of copper naphthenate, 20 gm. of 13 centipoises Parlon, 11.4 ml. of dibutyl phthalate, in 100 gm. of benzene.
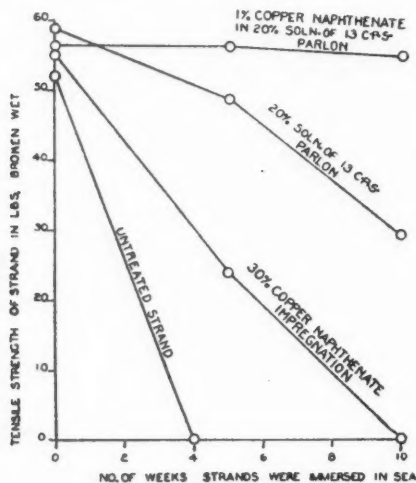
FIG. 6

## Wearing Quality of Treated Strands

Though the thickness of the Parlon film on the strand will be a factor determining the wearing quality of the strand, it was thought unnecessary to determine the relation between these two variables. The concentration of plasticizer in the Parlon film should also affect the wearing quality of the treated strand. The relation between these two variables is not easy to predict and therefore quantitative measurements on them were made.

Table VI shows the compositions of the Parlon solutions used to treat the strands. All treated strands were dried one week and the wearing quality

TABLE VI

WEARING QUALITY OF STRANDS

| Grams of 12 centipoises Parlon | Grams of benzene | Ml. of Aroclor No. 1242* | Wearing quality (No. of revolutions) | Increase in wearing quality due to Parlon film, % |
|---|---|---|---|---|
| Untreated strand | | | 21.3 | |
| 20 | 100 | 6 | 30.0 | 40.8 |
| 20 | 100 | 9 | 48.2 | 126.3 |
| 20 | 100 | 12 | 58.6 | 175.1 |
| 20 | 100 | 15 | 52.5 | 146.5 |
| 20 | 100 | 18 | 51.2 | 140.3 |

*"Aroclor No. 1242" is a trade name of a product manufactured by the Monsanto Chemical Company, St. Louis, U.S.A.

determinations made on the dried strands. Strands were not immersed in the sea. The measurements were made with the instrument illustrated in Fig. 1.

While Aroclor No. 1242 was used as a plasticizer here, it is doubtless true that very similar results would be found using dibutyl phthalate. It has been shown elsewhere in this paper that a proportion of 11.4 ml. of dibutyl phthalate to 20 gm. of 13 centipoises Parlon gave a film on the strand possessing maximum preservative quality. From the results of Table VI it is safe to conclude that such a concentration of dibutyl phthalate would produce a film having nearly optimum wearing quality.

### Flexibility of Treated Strands

The apparatus and procedure used are described elsewhere in this paper.

Table VII records not only the compositions of the impregnating solutions, but also the experimental results necessary for the calculation of flexibilities of treated strands. Treated strands were dried one week and the flexibilities determined on dry strands not immersed in the sea.

### TABLE VII

#### FLEXIBILITY OF STRANDS

| Cc. of dibutyl phthalate per 100 cc. of Parlon solution | Weights $(W_1, W_2, W_3)$, gm. | Time for pan to fall 3 cm. $(T_1, T_2, T_3)$, sec. |
|---|---|---|
| 7 | $W_1 = 75$ | $T_1 = 17.0$ |
| 7 | $W_2 = 70$ | $T_2 = 25.5$ |
| 7 | $W_3 = 65$ | $T_3 = 32.2$ |
| 8 | $W_1 = 70$ | $T_1 = 12.0$ |
| 8 | $W_2 = 65$ | $T_2 = 27.0$ |
| 8 | $W_3 = 60$ | $T_3 = 40.5$ |
| 9 | $W_1 = 57$ | $T_1 = 8.5$ |
| 9 | $W_2 = 50$ | $T_2 = 15.8$ |
| 9 | $W_3 = 42$ | $T_3 = 43.0$ |
| 10 | $W_1 = 42$ | $T_1 = 10.7$ |
| 10 | $W_2 = 37$ | $T_2 = 20.1$ |
| 10 | $W_3 = 42$ | $T_3 = 47.5$ |
| 11 | $W_1 = 33.0$ | $T_1 = 9.0$ |
| 11 | $W_2 = 30.0$ | $T_2 = 22.2$ |
| 11 | $W_3 = 27.0$ | $T_3 = 50.0$ |

Taking weight as ordinate and time as abscissa, the points $(W_1, T_1)$, $(W_2, T_2)$, $(W_3, T_3)$ were plotted for each of the five solutions of Column 1, Table VII. Five curves were obtained (see Fig. 7). On each of these five curves the weight $W_{25}$, corresponding to $T = 25$ sec., was read. This interpolated weight, $W_{25}$, has been arbitrarily defined to be the average flexibility of the treated strand. In Table VIII, Column 2, are given these average flexibilities for the five strands treated.
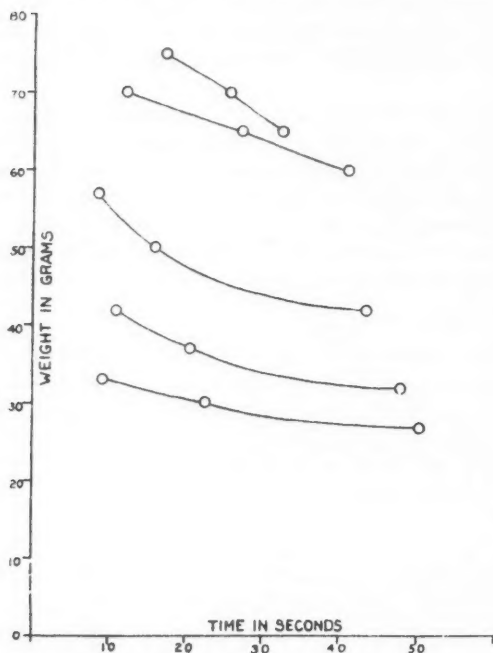
FIG. 7

## TABLE VIII

### AVERAGE FLEXIBILITY OF STRANDS

| Cc. of dibutyl phthalate per 100 cc. of Parlon solution | Average flexibility ($W_{25}$) at $T = 25$ sec., gm. | Cc. of dibutyl phthalate per 100 cc. of Parlon solution | Average flexibility ($W_{25}$) at $T = 25$ sec., gm. |
|---|---|---|---|
| 7 | 70.1 | 10 | 35.4 |
| 8 | 65.8 | 11 | 29.5 |
| 9 | 45.2 | | |

The concentration of plasticizer (dibutyl phthalate) was plotted against average flexibility (see Fig. 8). The value of this graph lies in our ability to determine from it the concentration of plasticizer required to produce any desired degree of flexibility.

Sea immersion tests showed that 9 cc. of dibutyl phthalate per 100 cc. of Parlon solution produces a preservative giving the treated strand a maximum life in the sea. Commercial fishermen have examined strands treated with the solution of 9 cc. of dibutyl phthalate per 100 cc. of Parlon solution, and
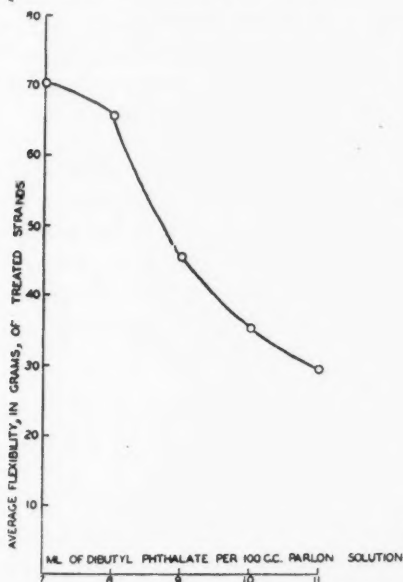
FIG. 8

are of the opinion that it is flexible enough for gill nets.  From the graph it is seen that this concentration of plasticizer produces an average flexibility of $W_{25} = 45.3$.  Until the preservative has been tested under actual fishing conditions, it seems advisable to work with a preservative producing a flexibility of about 45.  It is quite likely that tests to be made in the future under fishing conditions will show that somewhat greater flexibility will be necessary.  Such increase of flexibility must, unfortunately, be made at the expense of the length of life of the treated net in the sea.

*Treated Nets in Commercial Use*

While sea immersion tests of twine treated with preservatives are convenient, simple, and economical, they are at best useful for weeding out relatively poor preservatives from those showing promise.  Such tests do not give any indication of important requisites such as fishability of treated nets.  Hence it was decided to impregnate sections of gill net and have them sewed on to gill nets to be fished with for a season by commercial fishermen.  Only in this way could the real value of the various treatments be estimated, and unforeseen flaws be noticed.

Several commercial fishermen volunteered to sew into their nets sections of treated gill net.  The sections of gill net were identical in nature with the main net to which they were sewn.  The sections varied in size but an average one was 13 fathoms stretched and 50 meshes deep.  The type of gill net varied from 4/40 to 5/50.

The section was soaked for 30 min. in a solution of 15 gm. of 20 centipoises Parlon, 8.5 ml. of dibutyl phthalate (technical grade), 0.75 gm. of copper naphthenate per 100 gm. of benzene. Excess solution was then drained off and the section was spread out to dry, by suspending it from short wooden stakes for 24 hr. It was found important to spread out the treated section immediately after taking it from the Parlon solution, since the Parlon film soon becomes temporarily sticky and separation of the strands becomes difficult. Rubber gloves should be worn to prevent the hands from being coated with the sticky, but harmless, solution. The treated sections of net were then sewn on to the regular nets by the fishermen, who fished with them in the Pacific Coast waters during the summer of 1940. The fishermen treated the main body of their nets with various preservatives, chief of which was copper naphthenate.

The fishermen filled in questionnaires at the end of the 1940 season. For brevity, their reports are summarized. By "treated section" shall be meant the section of gill net treated with Parlon; by "regular net" shall be meant the main body of the gill net to which the treated section was sewn.

All found the treated section easier to handle than the regular net; the treated section was generally considered to remain quite clean and easy to wash; all reported an equal catch of fish per unit area for treated section and regular net; only one fisherman desired greater flexibility of treated section. In no particular respect was the treated section considered inferior to nets impregnated with other commonly used preservatives, but rather the fishermen were definitely pleased with the treatment. The strength of the treated section was judged to be only slightly greater than that of the regular net after a summer's fishing. Measurements made by the authors confirmed this conclusion of the fishermen.

The above summary enables two very important conclusions to be drawn. First, a net treated with Parlon solution has several attractive properties possessed in a much lesser degree by a net treated with the commonly used preservatives, cutch, linseed oil, and copper naphthenate. Second, the Parlon treatment as it now stands does not retard rotting of a net to a much greater degree than copper naphthenate, a result not at all in agreement with the laboratory tensile strength measurements on treated twine. This was undoubtedly due to the fact that the Parlon solution did not penetrate into the knots sufficiently. This drawback probably can be overcome by treating the twine prior to weaving the net, and this method of treatment is now under study. Together with this investigation, there is being studied a promising method of actually increasing penetration of the Parlon solution into the knots of the net. In this latter investigation sea immersion tests are being conducted on sections of treated gill net, instead of twine. A solvent very much cheaper than benzene is also being investigated. Large-scale tests by fishermen will then be made.

*Cost of Treating a Net with Parlon Solution*

With benzene as a solvent, it costs between $12 and $14 to treat a complete net, using a solution of 15 gm. of 20 centipoises Parlon and 8.5 ml. of dibutyl phthalate per 100 gm. of benzene—approximately 10% of the prewar price of the net.

## Summary

(1) A new instrument for measuring flexibility of strands has been devised.

(2) Several organic solvents have been shown to be without effect on the tensile strength of strands of 5/40 linen.

(3) Gum chicle, gutta percha, and pale crepe were chlorinated. Products containing various amounts of chlorine were obtained, by chlorinating for different periods of time, and at different temperatures. These products were used as preservatives of 5/40 linen twine. Parlon, the commercially produced chlorinated rubber, was also tested, simultaneously. The tensile strengths of the treated strands, after several weeks' immersion in the sea, showed all products from chlorination of gum chicle and gutta percha to be useless as preservatives, and the product of the chlorination of pale crepe to be as effective, but not more so, than Parlon.

(4) The addition of a plasticizer to the chlorinated rubber was found to be essential, in order that the treated strand would have the necessary degree of flexibility. After a strand of 5/40 linen, impregnated with Parlon plasticizer (dibutyl phthalate), had been immersed in the sea for several weeks its tensile strength was found to be a function of the concentration of plasticizer. An optimum concentration of plasticizer exists, at which concentration the life of a strand in the sea is greatest.

(5) For all concentrations of Parlon in benzene, and for all concentrations of plasticizer (dibutyl phthalate) of any practical value, no knot slippage occurs.

(6) The most effective preservative found consists of an impregnating solution with the composition:—

| | |
|---|---|
| Parlon (13 centipoises) | 20 gm. |
| Dibutyl phthalate | 11 to 11.5 cc. |
| Benzene | 100 gm. |
| Copper naphthenate | 1 gm. |

Stated more generally, the ratio of number of cubic centimetres of dibutyl phthalate to grams of Parlon is 0.56 for 13 centipoises Parlon. This ratio most probably applies to Parlon of viscosity 10 to 20 centipoises.

(7) Tests were conducted under actual fishing conditions. Sections of treated net were sewn with regular nets and fished with for a season. Results show that the Parlon preservative has many attractive features, but that further work is required in order to ensure greater penetration of the Parlon solution into the knots of the net.

## Acknowledgments

It is a pleasure to acknowledge the assistance given by the following: The Canadian Fishing Company, Vancouver, for the use of their tensile strength machine; the Physics Department of this University for constructing the flexibility apparatus; the Hercules Powder Company, Inc., Wilmington, Delaware, U.S.A., for furnishing samples of Parlon. To many fishermen especial thanks are due for their suggestions and co-operation in large-scale tests on treated sections of net.

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